



NIST Gradient Flow Coater

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Why is thickness so important?

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- ❑ Film thickness is a critical parameter in many applications
 - ❑ self-assembly of block copolymers
 - ❑ film stability / dewetting
 - ❑ pressure sensitive adhesives
 - ❑ fundamental polymer physics
 - ❑ barrier coatings
 - ❑ photoresists / imprint resists
 - ❑ electronic packaging
 - ❑ advanced coatings
- ❑ Offers a rich parameter space to probe material properties and response surfaces
- ❑ NIST flow coater opens the window to combinatorial libraries of film thickness in the range of nm to μm

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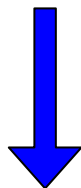


Flow coating - basics

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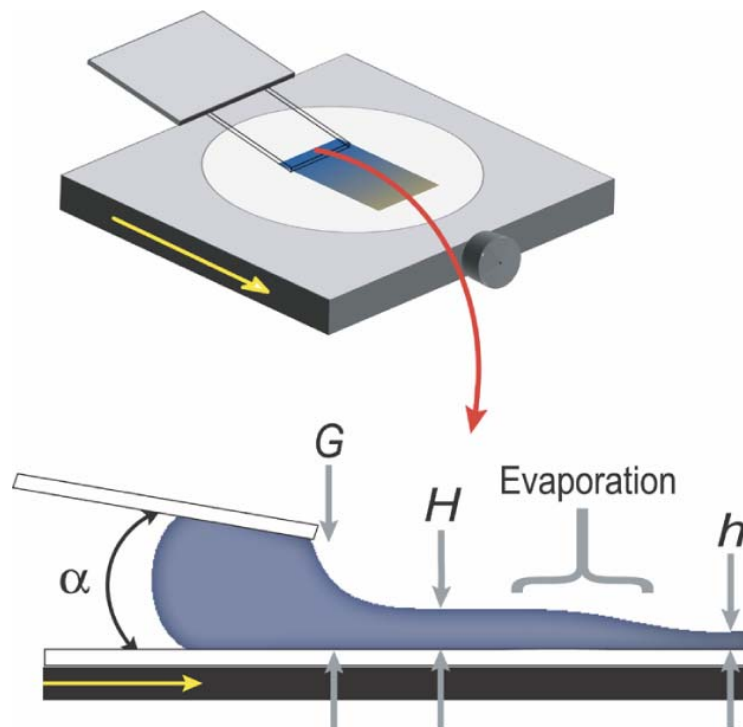
- Capillary forces hold polymer solution between a stationary knife blade and a substrate
- Frictional drag is exerted on the solution as blade accelerates over substrate



Low ν \rightarrow capillary forces win
thinner films

High ν \rightarrow drag wins
thicker films

Acceleration yields **thickness gradient**

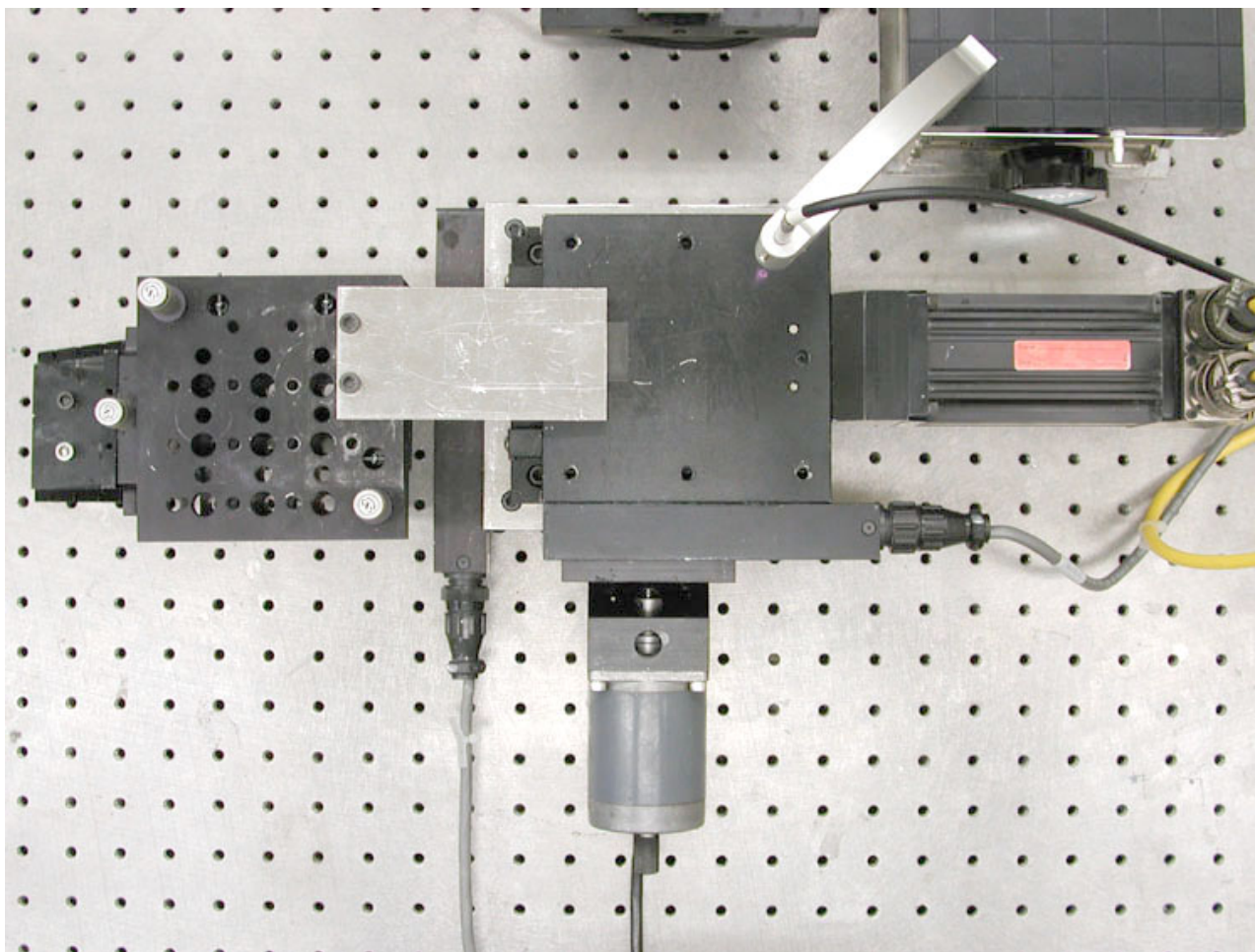




NCMC flow coater

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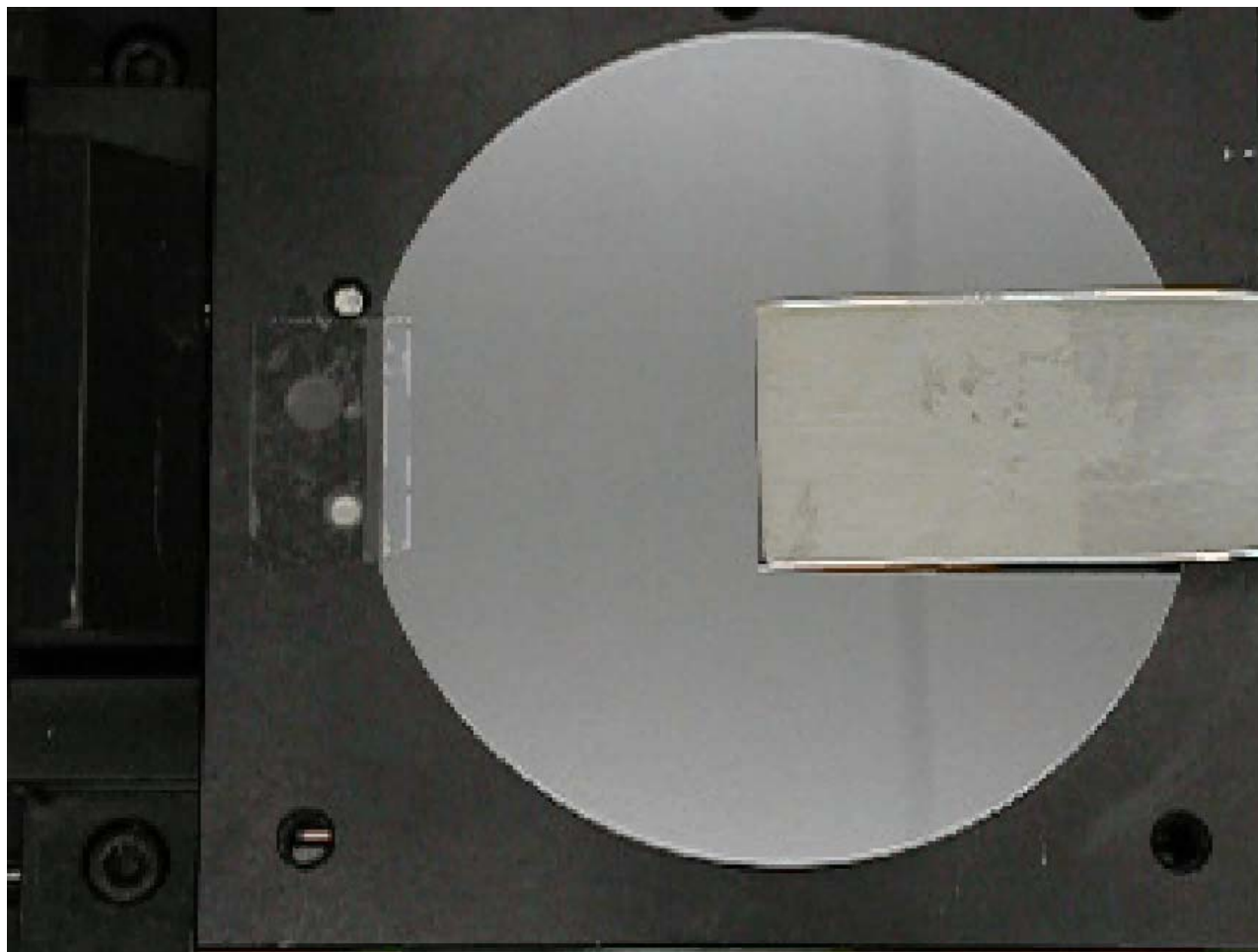
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Flow coating - in action

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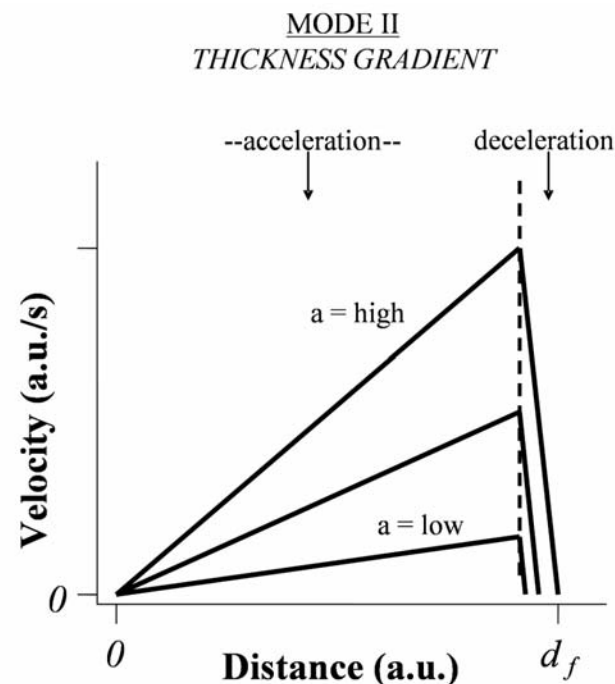
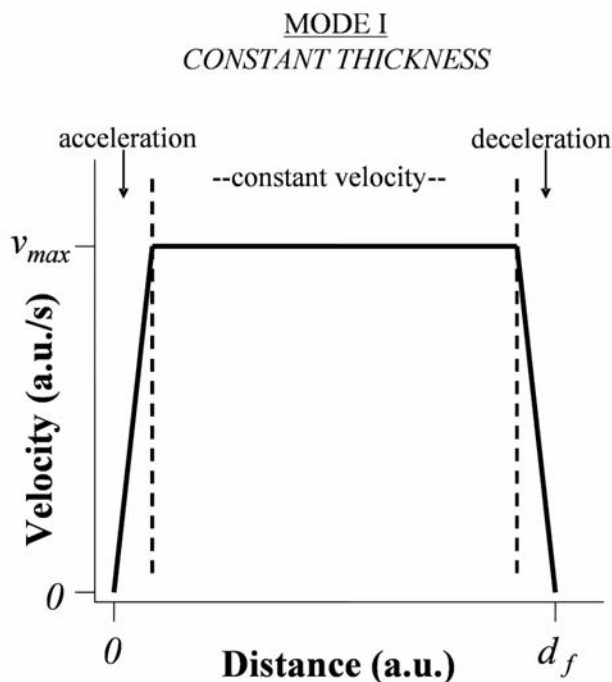
Velocity profiles

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□ Mode 1: Uniform Film Thickness

- Acceleration is set very high
- Thickness dictated by maximum stage velocity (input v_{max})



□ Mode 2: Thickness Gradient Films

- Acceleration is set low
- Thickness dictated by instantaneous velocity (controlled by a)



Flow coating - quantifying

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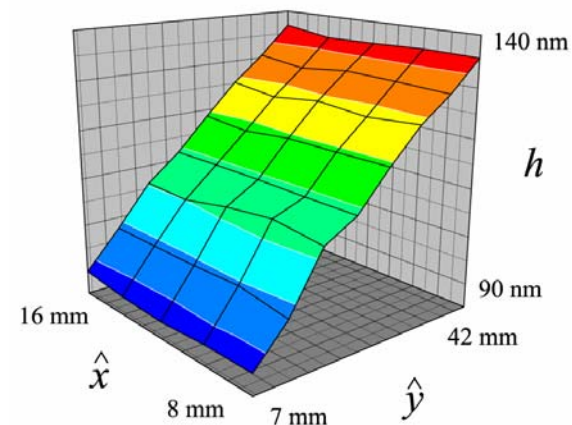
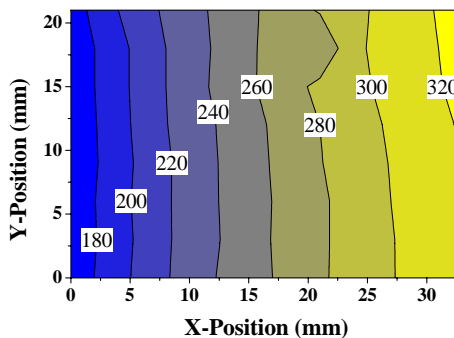
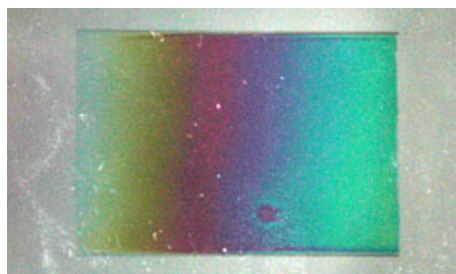
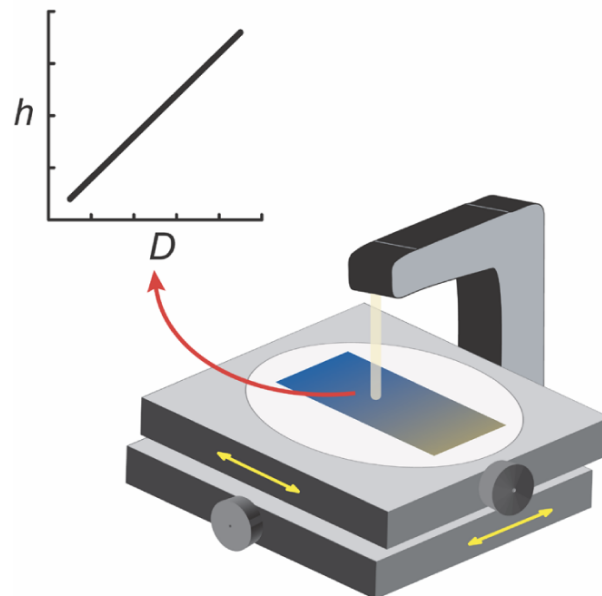
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- Measurement - thickness
- Thickness measured via:
 - Interferometry
 - Ellipsometry
 - Profilometry
- Visualization
 - Contour plots
 - Surface plots



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Generating thickness gradients of thin polymer films via flow coating

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Thickness is a governing factor in the behavior of films and coatings. To enable the high-throughput analysis of this parameter in polymer systems, we detail the design and operation of a "flow coater" device for fabricating continuous libraries of polymer film thickness over tailored ranges. Focusing on the production of model polystyrene film libraries, we thoroughly outline the performance of flow coating by varying critical factors including device geometry, device motion, and polymer solution parameters. [DOI: 10.1063/1.2173072]

I. INTRODUCTION

The advent of combinatorial and high-throughput techniques for drug discovery,¹ and more recently for materials science,² has illuminated the power of these methods for accelerating product discovery and functional knowledge generation. Combinatorial and high-throughput methodologies depend upon the ability to fabricate specimen libraries that systematically survey parameters of interest over wide ranges. For materials science, this entails producing libraries that spatially vary factors governing performance and behavior, such as composition and processing parameters. There are two main paradigms for materials library design and fabrication. Discrete libraries consist of a collection of distinct subspecimens arranged in an orderly array. Discrete libraries offer wide surveys of large parameter spaces, but fabrication of these arrays often involves an extensive robotics infrastructure. In contrast, *gradient* libraries (considered in this work) exhibit a gradual and continuous change in one or more parameters as a function of position. By their nature, gradient specimens have a limited scope; however, such libraries offer an unparalleled means for thoroughly mapping material behavior over a specific range of parameter space and for exactly identifying critical phenomena such as phase boundaries. Moreover, as discussed below, gradient libraries can be produced with a modest investment in equipment.

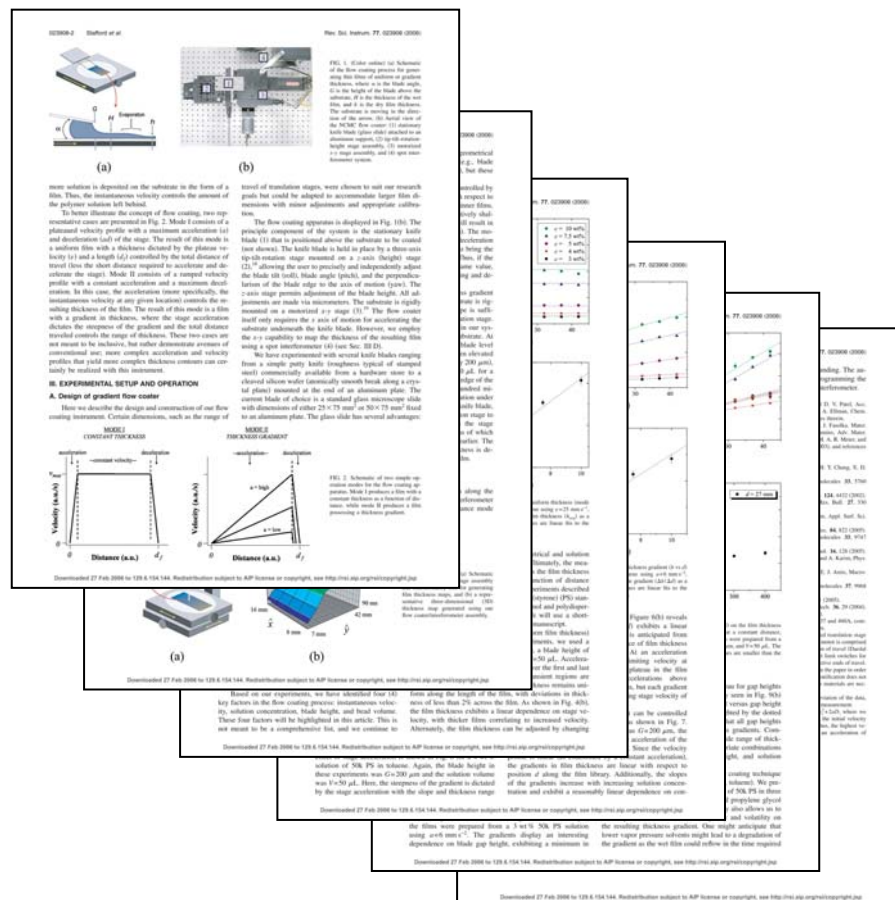
Beginning with the seminal work of Hanak,³ materials researchers from several groups have introduced methods for fabricating continuous gradients in a variety of parameters, such as composition,^{4,5} temperature,^{6,7} surface energy,^{7,8} and UV exposure.⁹ In concert with this growing body of research, this article considers a method for creating continuous gradient libraries in polymer film thickness. In the context of a combinatorial workflow, steep gradients provide a broad survey of a phenomenon or process over a large parameter space while shallow gradients offer access to finer details and higher resolution measurements. Our apparatus, which we have termed a "flow coater," has been demon-

strated in previous work from our group and others. These former studies applied the device to map the effect of film thickness on phenomena such as wetting,^{10,11} block copolymer morphology,^{12,13} and crazing/fracture.^{14,15} In the current article, we detail the design and operation of our flow coater. In particular, we provide an extensive set of data that demonstrates the performance of the instrument over a variety of critical factors including device geometry, device motion, and polymer solution parameters.

II. DEVICE CONCEPTS

Flow coating is ideal for generating gradients in polymer film thickness in the submicron regime. The apparatus, illustrated in Fig. 1, consists of a stationary knife blade fixed at some distance (gap height) above a movable stage. Typical gap heights range from tens of microns to hundreds of microns. The substrate to be coated is rigidly fixed to the stage, and a bead of polymer solution is deposited/wicked between the blade and the substrate. The blade is then accelerated with respect to the substrate. The flow coating process draws upon a competition between (1) capillary forces holding the polymer solution between the stationary knife blade and the substrate, and (2) frictional drag exerted on that same solution as the blade is pulled across the substrate. Flow coating is similar in concept to other metered flows such as dip coating and blade coating. Readers are referred to several review articles^{16,17} for details and further references on the various types of coating flows. However, an exact fluid mechanics model that best represents the flow dynamics encountered in our process has yet to be developed, and we are currently generating an appropriate theoretical model to predict the flow coating behavior documented in this work.

In flow coating, capillary forces hold the polymer solution under the blade at the initial condition of zero velocity; over time, the volume will slowly decrease due to evaporation of solvent from the edges. At low velocities, capillary forces still aim to keep the material between the substrate and the blade, but frictional drag causes some solution to escape under the knife blade. This material is left behind in the form of a wet film, which then dries by solvent evaporation. At higher velocities, the frictional drag increases and



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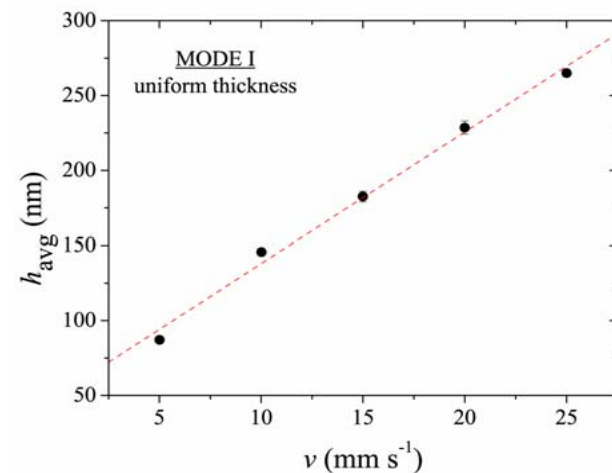
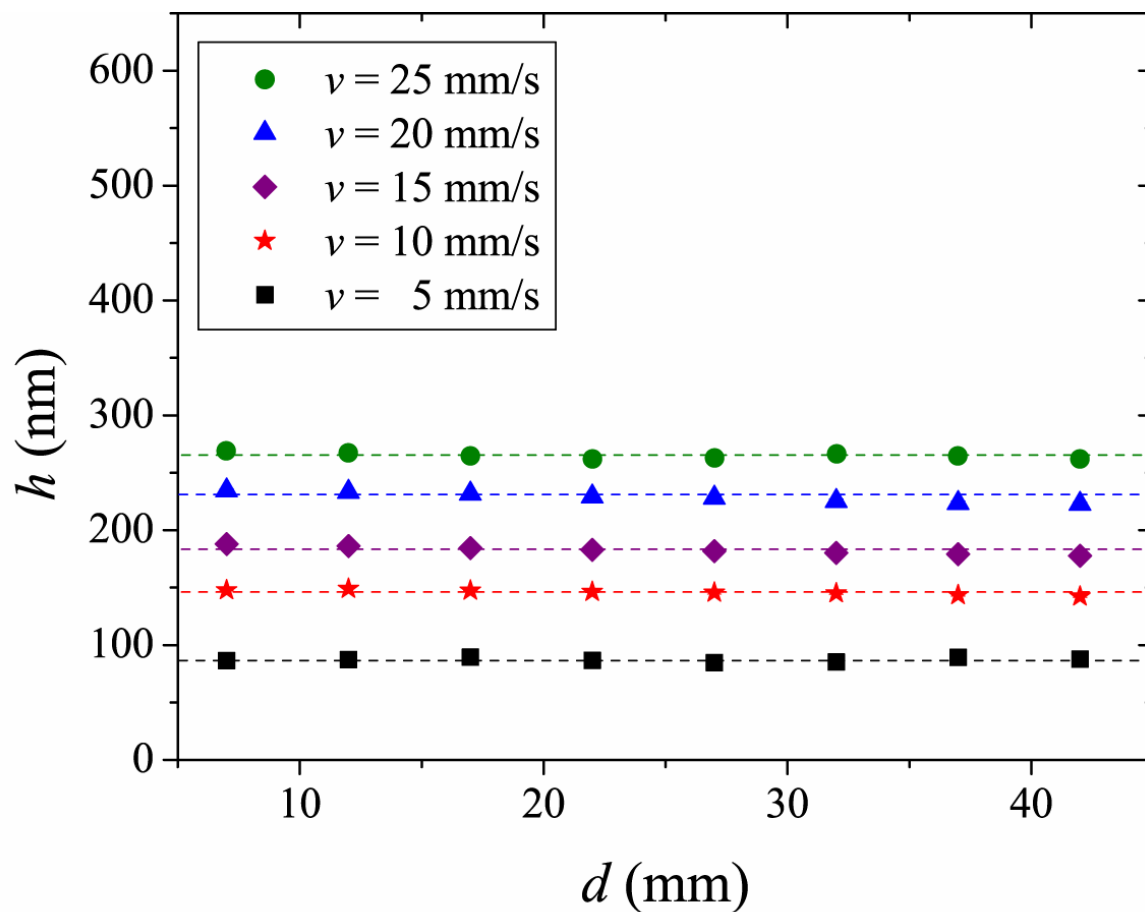


Mode I - constant thickness

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Thickness is linear with velocity. Good start!



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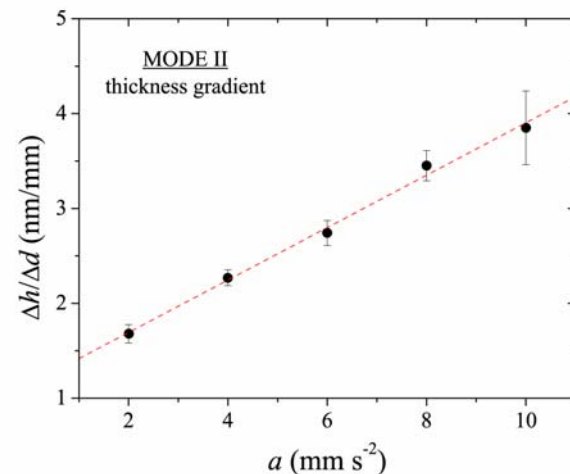
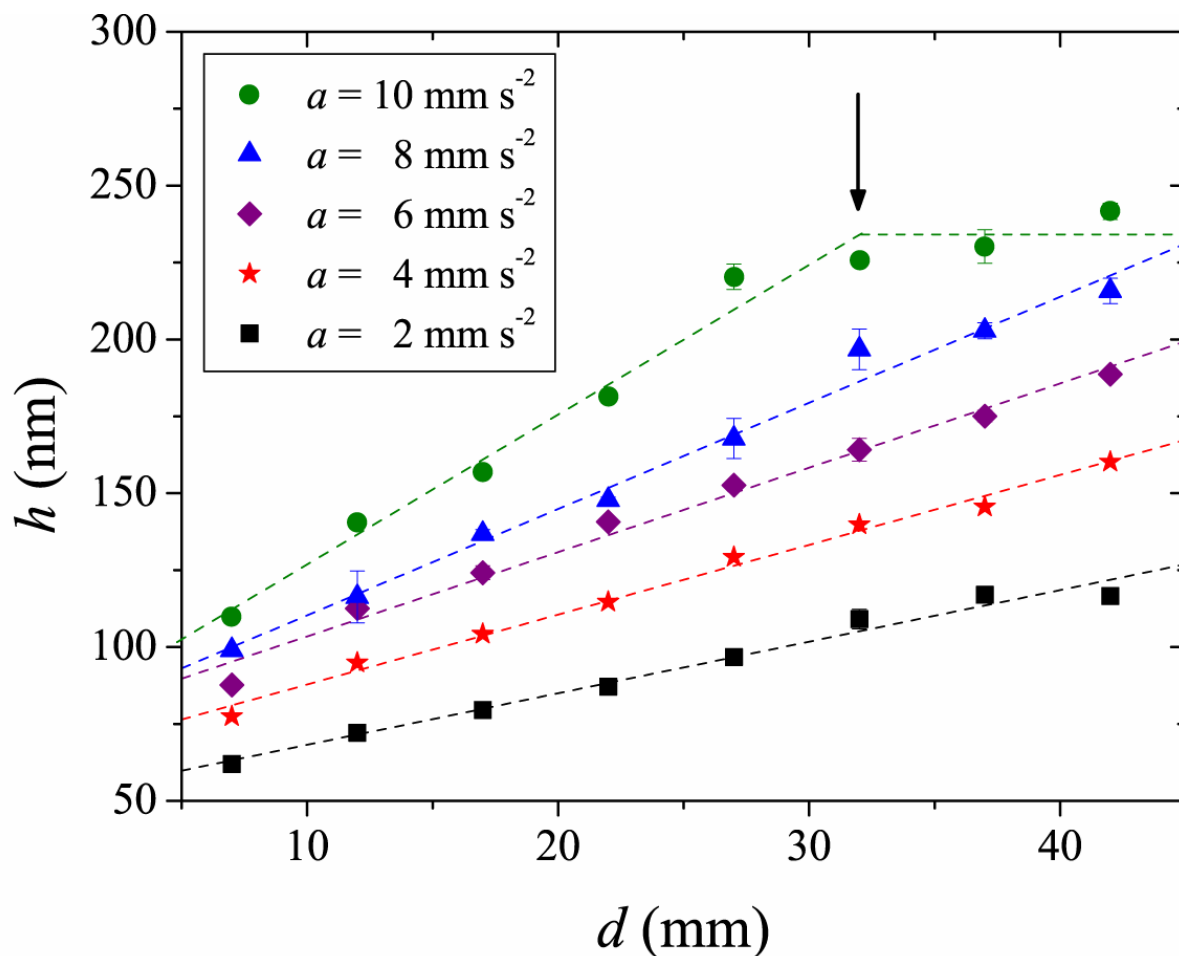


Mode II - thickness gradient

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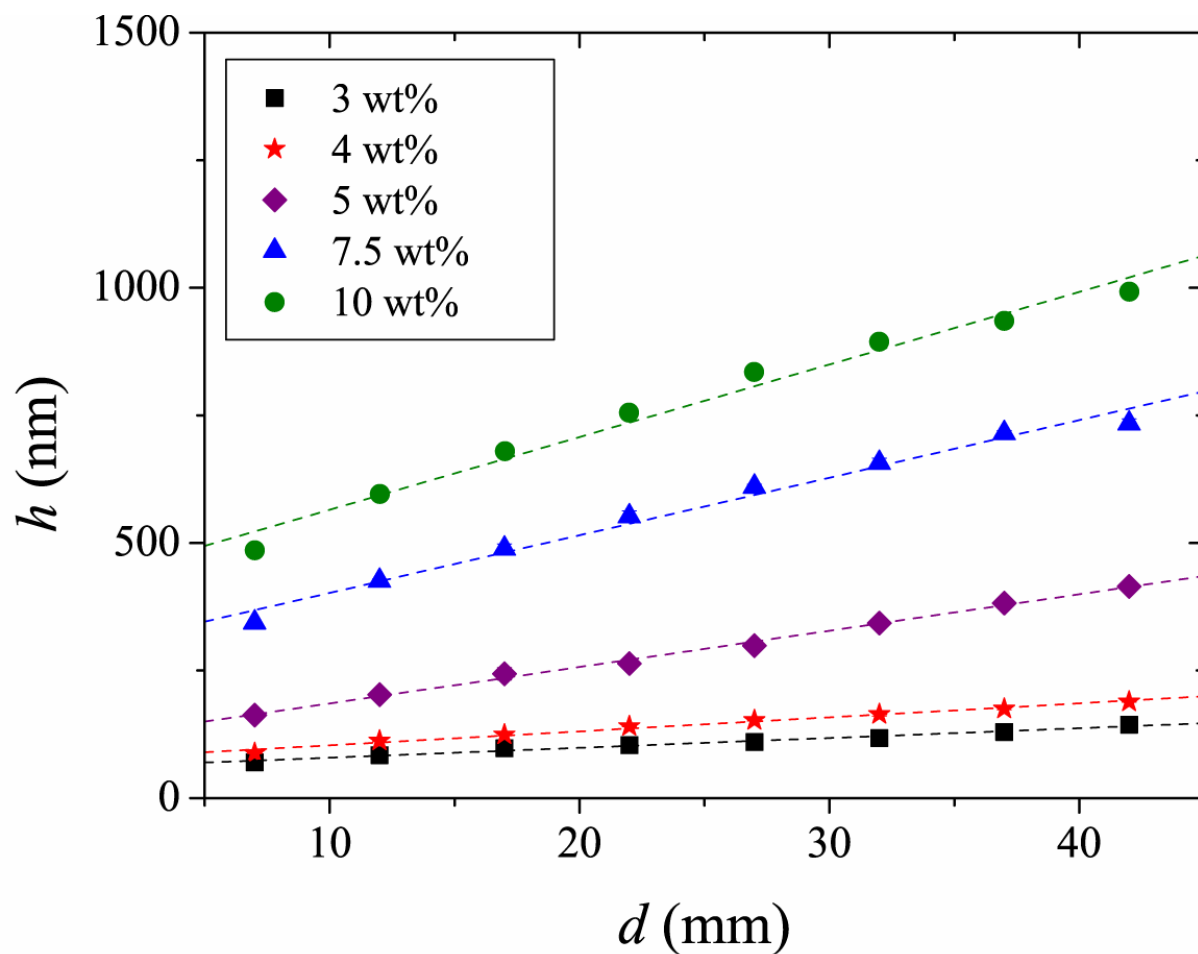
Since thickness is linear with velocity, gradient should also be linear with distance (instantaneous velocity).





Mode II - concentration

Thickness gradient can go from 10s of nanometers to several microns.
We have not explored the upper limit to the technique yet.



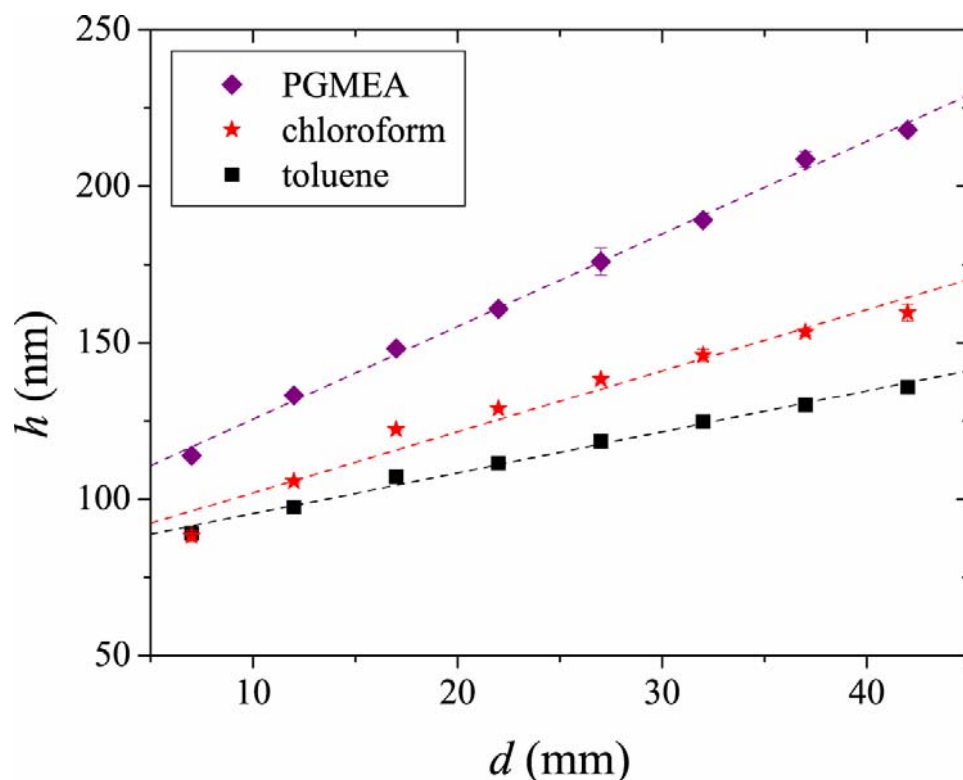


Mode II - solvent volatility

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| solvent | b.p. (°C) | v. p. @ 20 °C (mm Hg) | ρ (g mL ⁻¹) | η @ 20 °C (cP) |
|------------|--------------|--------------------------|---------------------------------|------------------------|
| Chloroform | 60.5 - 61.5 | 160 | 1.492 | 0.58 |
| Toluene | 110 - 111 | 22 | 0.865 | 0.59 |
| PGMEA | 145 - 146 | 3.7 | 0.970 | 1.31 |



← Drying time on the order of minutes

← Drying time on the order of seconds

All solutions had same wt% polymer.

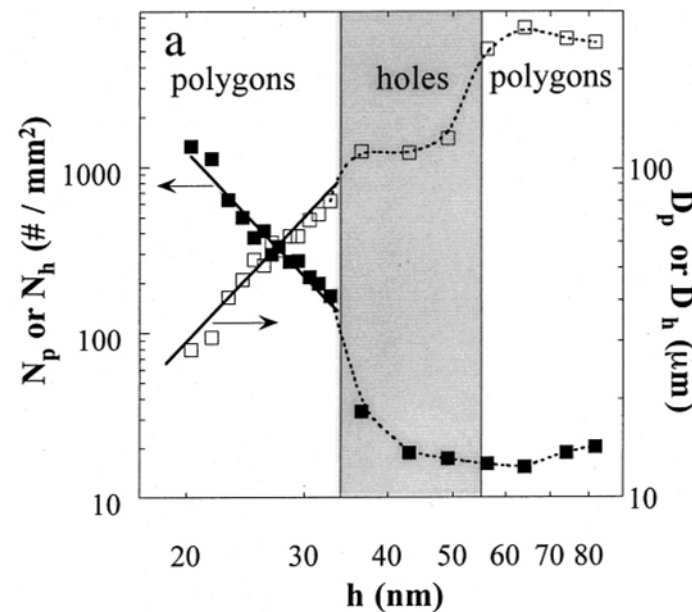
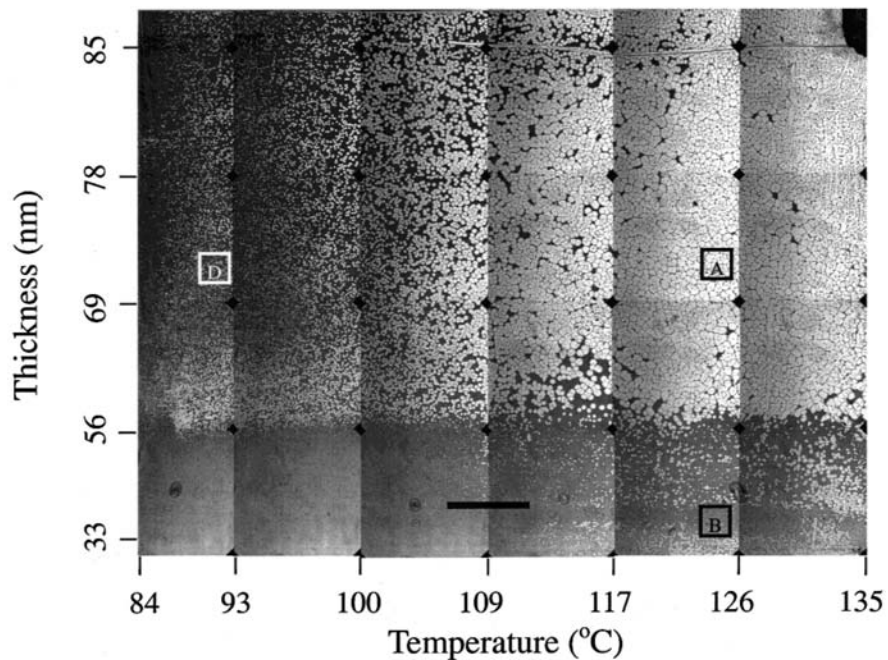
Solution viscosity very different!!



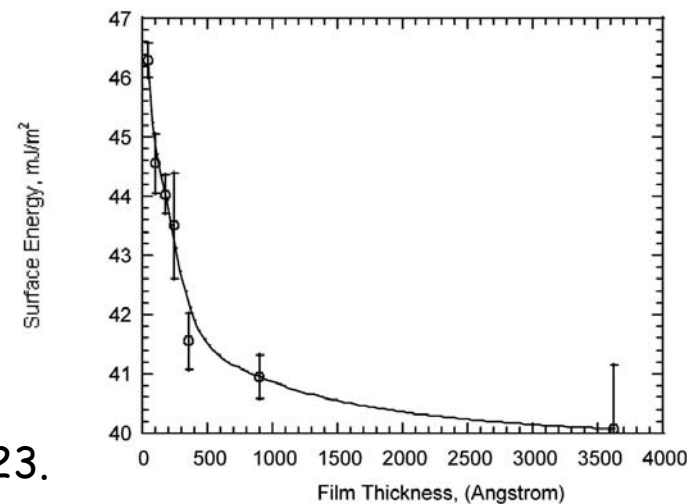
Applications - film stability

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Meredith et al. *Macromolecules* **2000**, *33*, 9747-9756.



Ashley et al. *Langmuir* **2005**, *21*, 9518-9523.



Applications - crystallization

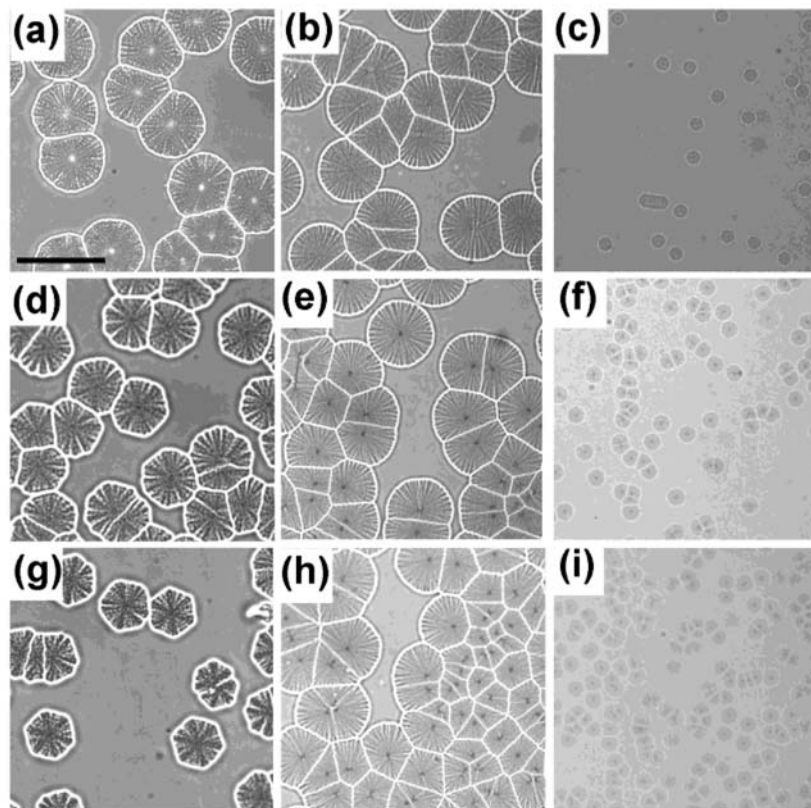
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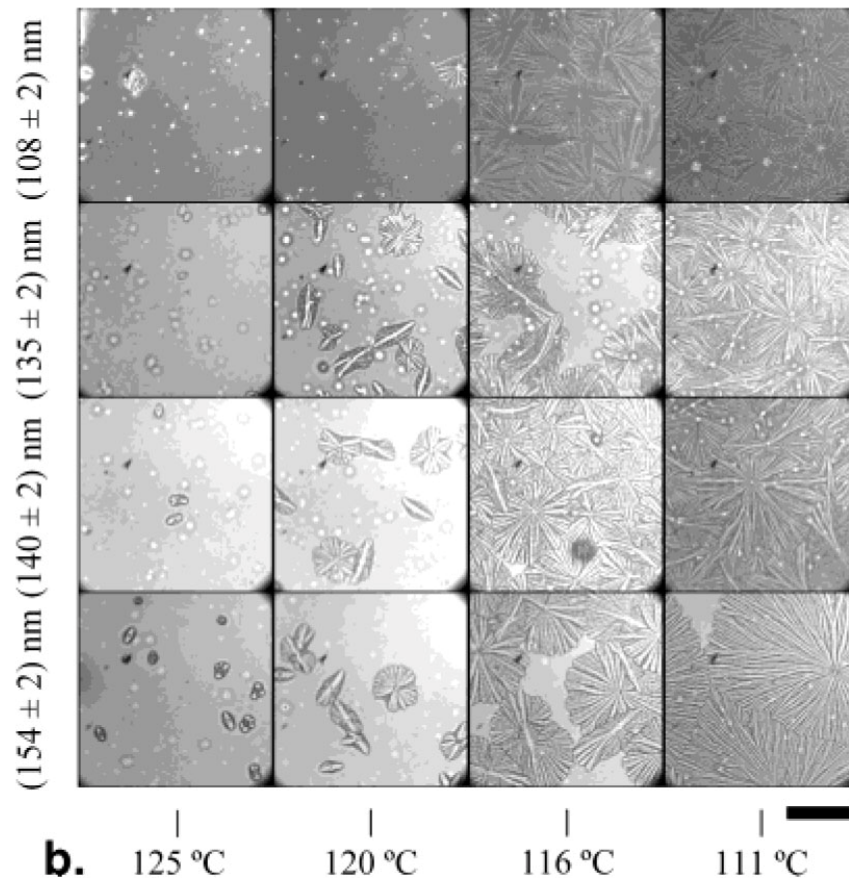
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Beers et al. *Langmuir* **2003**, *19*, 3935-3940.



Walker et al. *Langmuir* **2003**, *19*, 6582-6585.



Applications - BCP morphology

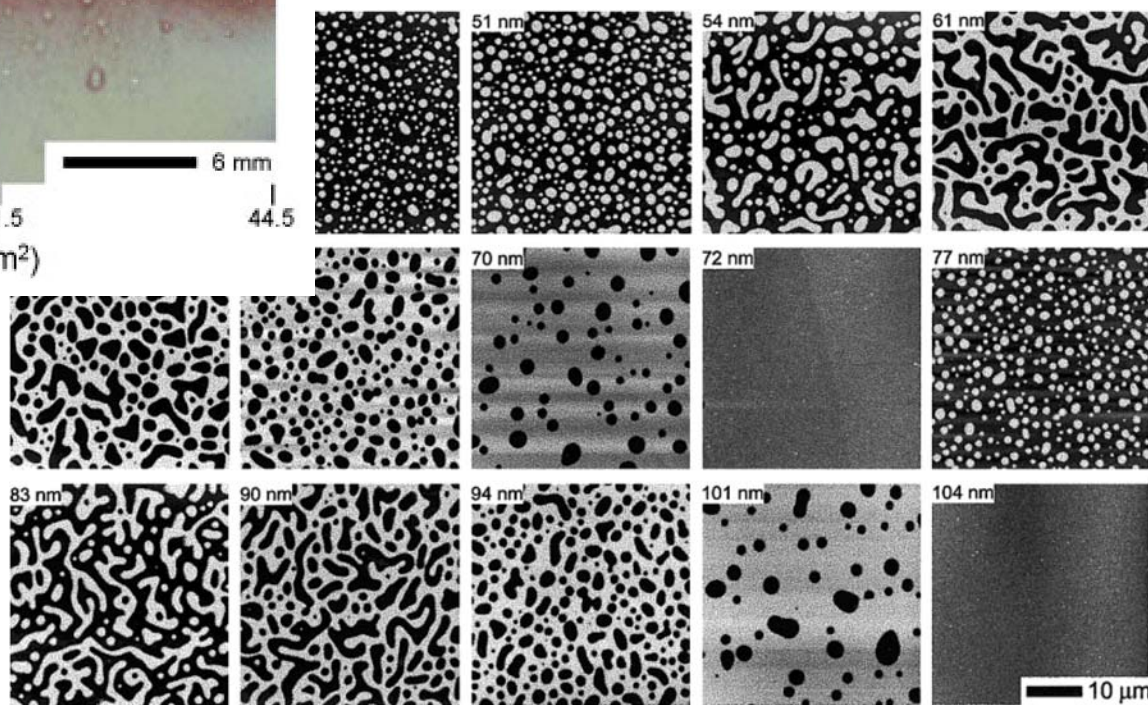
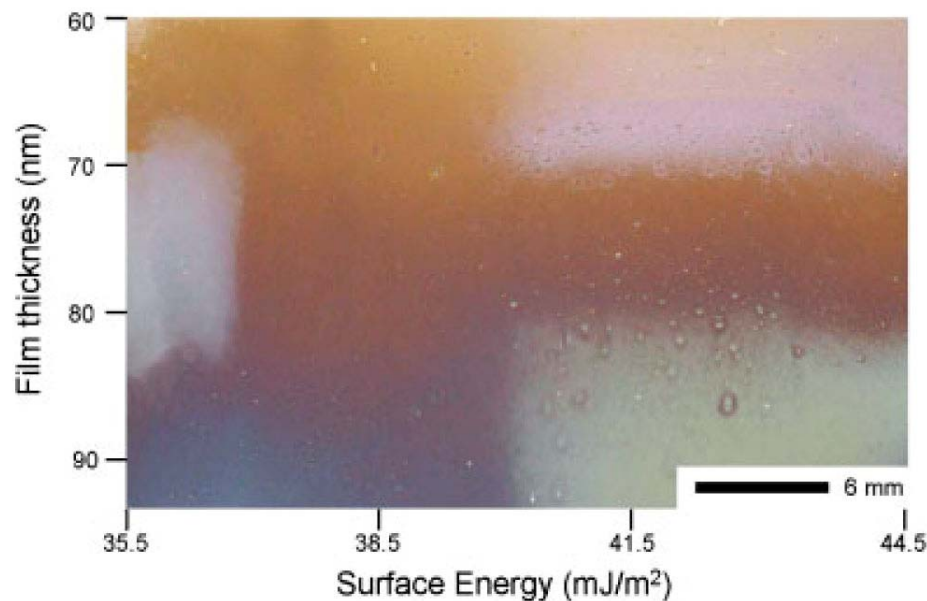
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Smith et al. *J. Polym. Sci. B: Polym. Phys.* **2001**, *39*, 2141-2158.
Smith et al. *Phys. Rev. Lett.* **2001**, *87*, 015503.



Flow coating - next generation

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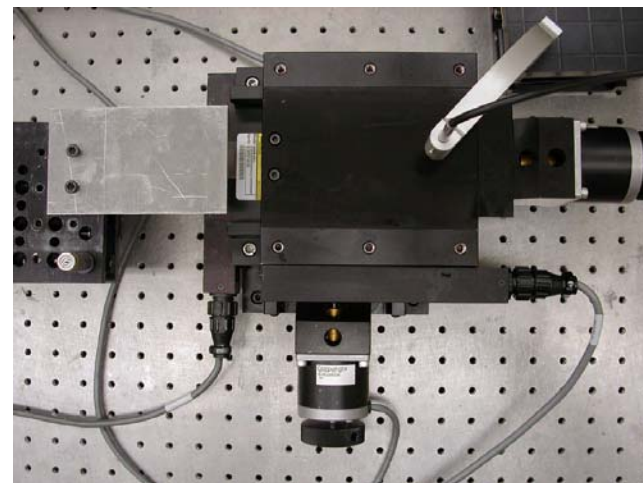
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- ❑ New stages
 - ❑ Longer range of travel (100 mm)
 - ❑ Higher velocities (63 mm/s)
 - ❑ Limit / home switches
 - ❑ Single motion controller
- ❑ Flow coater only requires one stage; second stage provides mapping capabilities
- ❑ Total cost - \$15k
 - ❑ stages
 - ❑ motion controllers
 - ❑ PCI card
 - ❑ tip/tilt stage and brackets



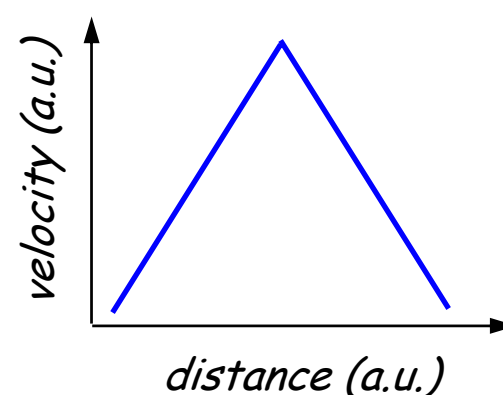
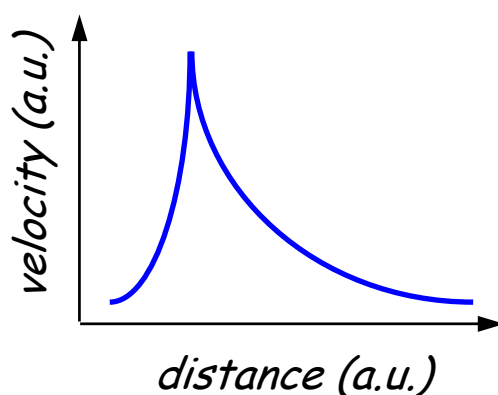
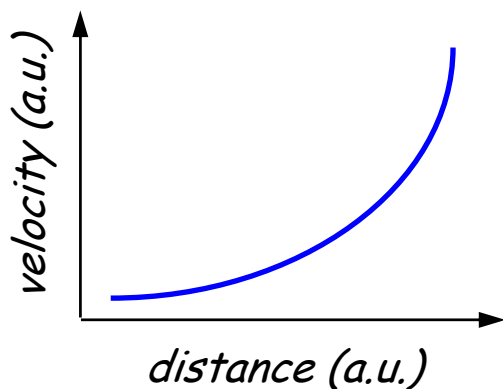


Future Work

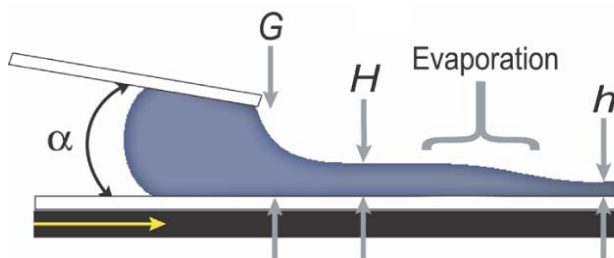
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- Develop model for coating flows in this geometry
- Explore upper limit of thickness regime
- Non-linear acceleration profiles



- Other geometrical factors





Future Work

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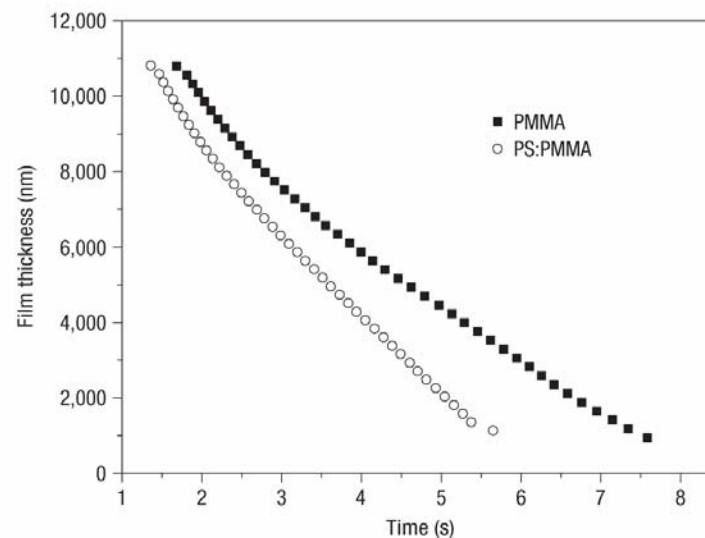
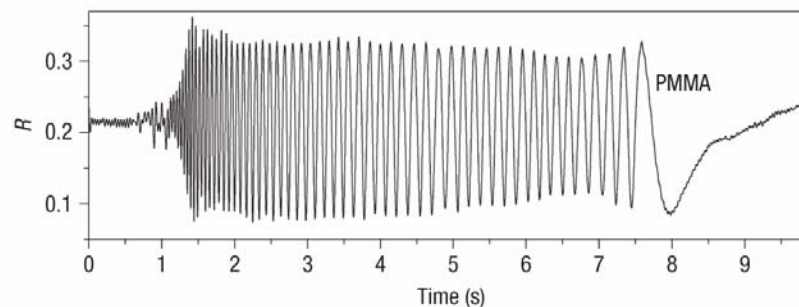
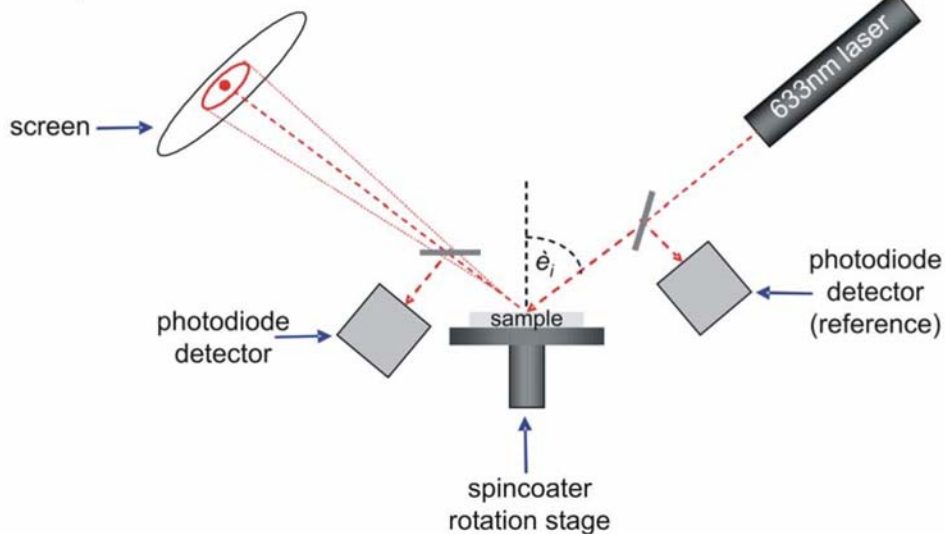
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- We know the gap height and final film thickness.
- But we are blind to everything that happens in-between.
- Specular reflectivity \rightarrow answers.



S.Y. Heriot and R.A.L. Jones, *Nat. Mater.* **2005**, *4*, 782-786.



Conclusions

- ❑ NCMC flow coater is a versatile combinatorial tool
- ❑ Can generate thickness gradients ranging from 10 nm to 10 μm
- ❑ We have started benchmark tests
- ❑ Benchmarks will validate the coating flow model

Acknowledgments

- ❑ Wenhua Zhang & Xuesong Hu - Python motion control
- ❑ Kristen Roskov - SURF student